

# PATENT COOPERATION TREATY

## PCT

### INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY (Chapter II of the Patent Cooperation Treaty)

(PCT Article 36 and Rule 70)

REC'D 24 APR 2006

WIPO

PCT

Applicant's or agent's file reference <b>010941-0003</b>	<b>FOR FURTHER ACTION</b>		See Form PCT/IPEA/416
International application No. <b>PCT/CA2004/002147</b>	International filing date (day/month/year) 16 December 2004 (16-12-2004)	Priority date (day/month/year) 17 December 2003 (17-12-2003)	
International Patent Classification (IPC) or national classification and IPC IPC: <b>C09C 1/22</b> (2006.01), <b>C09C 3/00</b> (2006.01), <b>C22B 7/02</b> (2006.01), <b>C22B 3/04</b> (2006.01), <b>C09C 1/00</b> (2006.01)			
Applicant <b>FERMAG INC. ET AL</b>			
1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36. 2. This REPORT consists of a total of <u>6</u> sheets, including this cover sheet. 3. This report is also accompanied by ANNEXES, comprising: a. <input checked="" type="checkbox"/> (sent to the applicant and to the International Bureau) a total of <u>19</u> sheets, as follows: <input checked="" type="checkbox"/> sheets of the description, claims and/or drawings which have been amended and are the basis of this report and/or sheets containing rectifications authorized by this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions). <input type="checkbox"/> sheets which supersede earlier sheets, but which this Authority considers contain an amendment that goes beyond the disclosure in the international application as filed, as indicated in item 4 of Box No. 1 and the Supplemental Box. b. <input type="checkbox"/> (sent to the International Bureau only) a total of (indicate type and number of electronic carrier(s)) , containing a sequence listing and/or tables related thereto, in electronic form only, as indicated in the Supplemental Box Relating to Sequence Listing (see Section 802 of the Administrative Instructions). 4. This report contains indications relating to the following items: <input checked="" type="checkbox"/> Box No. I      Basis of the report <input type="checkbox"/> Box No. II     Priority <input type="checkbox"/> Box No. III    Non-establishment of opinion with regard to novelty, inventive step and industrial applicability <input type="checkbox"/> Box No. IV     Lack of unity of invention <input checked="" type="checkbox"/> Box No. V      Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement <input type="checkbox"/> Box No. VI     Certain documents cited <input checked="" type="checkbox"/> Box No. VII    Certain defects in the international application <input checked="" type="checkbox"/> Box No. VIII   Certain observations on the international application			
Date of submission of the demand <b>04 July 2005 (04-07-2005)</b>		Date of completion of this report <b>18 April 2006 (18-04-2006)</b>	
Name and mailing address of the IPEA/CA Canadian Intellectual Property Office Place du Portage I, C114 - 1st Floor, Box PCT 50 Victoria Street Gatineau, Quebec K1A 0C9 Facsimile No.: 001(819)953-2476		Authorized officer  <b>Sonia John (819) 934-3599</b>	

# INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

International application No.  
PCT/CA2004/002147

## Box No. I Basis of the report

1. With regard to the **language**, this report is based on:
  - ☒ the international application in the language in which it was filed
  - ☐ a translation of the international application into \_\_\_\_\_, which is the language of a translation furnished for the purposes of:
    - ☐ international search (Rules 12.3(a) and 23.1(b))
    - ☐ publication of the international application (Rule 12.4(a))
    - ☐ international preliminary examination (Rules 55.2(a) and/or 55.3(a))
2. With regard to the **elements** of the international application, this report is based on *(replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report)*:
  - ☐ the international application as originally filed/furnished
  - ☒ the description:
    - ☒ pages 2, 3, 5-9, 11, 13, 15, 17-26, 29-32, 34-39, 42-54 as originally filed/furnished
    - ☒ pages\* 1, 4, 10, 12, 14, 16, 27, 28, received by this Authority 04 July 2005 (04-07-2005)
    - ☐ pages\* received by this Authority
  - ☒ the claims:
    - ☐ pages as originally filed/furnished
    - ☐ pages\* as amended (together with any statement) under Article 19
    - ☒ pages\* 55-59 received by this Authority 04 July 2005 (04-07-2005)
    - ☐ pages\* received by this Authority
  - ☒ the drawings:
    - ☒ pages 4/23 - 23/23 as originally filed/furnished
    - ☐ pages\* received by this Authority on
    - ☒ pages\* 1/23 - 3/23 received by this Authority 04 July 2005 (04-07-2005)
  - ☐ a sequence listing and/or any related table(s) - see Supplemental Box Relating to Sequence Listing.
3. ☐ The amendments have resulted in the cancellation of:
  - ☐ the description, pages
  - ☐ the claims, Nos.
  - ☐ the drawings, sheets/figs
  - ☐ the sequence listing *(specify)*:
  - ☐ any table(s) related to sequence listing *(specify)*:
4. ☐ This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).
  - ☐ the description, pages
  - ☐ the claims, Nos.
  - ☐ the drawings, sheets/figs
  - ☐ the sequence listing *(specify)*:
  - ☐ any table(s) related to sequence listing *(specify)*:

\* If item 4 applies, some or all of those sheets may be marked "superseded."

**Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement****1. Statement**

Novelty (N)	Claims	1-22	YES
	Claims	23-30	NO
Inventive step (IS)	Claims	1-22	YES
	Claims	23-30	NO
Industrial applicability (IA)	Claims	1-30	YES
	Claims	NONE	NO

**2. Citations and explanations (Rule 70.7)**

- D1:** JEBRAK MICHEL, MAURICE MORENCY and DENISE FONTAINE:  
"Caracterisation et technologie de traitement des poussières d'acierage a Sorel -Tracy",  
Quebec Department of the Environment - St. Lawrence Centre, Environment Canada, March 1993
- D2:** CA 1184363 A (BAYER AKTIENGESELLSCHAFT) 26 March 1985 (26-03-1985)
- D3:** CA 1331274 C (BAYER AKTIENGESELLSCHAFT) 09 August 1994 (09-08-1994)
- D4:** CA 1186885 A (BAYER AKTIENGESELLSCHAFT) 14 May 1985 (14-05-1985)

**Novelty (N)**

Claims 1-22 comply with **PCT Article 33(2)**. Document D1 is considered as describing the closest prior art, however, since D1 does not disclose that an anionic surfactant is added to the slurry to disperse the ferrite particles adsorbed on the magnetite particles, the subject matter of claim 1 is novel. Claims 2-22 are dependent on claim 1 and, as such, are also considered novel.

Claims 23-26 and 29 do not comply with **PCT Article 33(2)**. The subject matter was disclosed before the claim date in D2. D2 discloses a ferrite pigment and its use as a pigment in organic binders, plastics, building materials, paper, ceramic, and anti-corrosion paints. Although the ferrite pigment disclosed in D2 is not manufactured from an EAF dust, no advantages have been disclosed in the present invention to show that a ferrite pigment manufactured from an EAF dust would have any advantages over a ferrite pigment manufactured in any other way. Furthermore, "coming from an EAF dust" is not a property of the ferrite pigment but rather a property of the process to produce the ferrite pigment. Also, a ferrite pigment having a resistance to leaching is not new as all ferrite pigments must have some degree of resistance to leaching otherwise the pigment would not be useful and the word "high" cannot be used to distinguish the present invention from the prior art since the word "high" is a relative term and is thus unclear. Ferrite pigments are known in the art and an allegedly new method of manufacture does not bestow patentability on an old product. Therefore claims 23-26 and 29 are not novel.

*See Supplemental Box for further details*

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

International application No.  
PCT/CA2004/002147

Box No. VII Certain defects in the international application

The following defects in the form or contents of the international application have been noted:

On page 23, line 5, "alcaline" should be written as "alkaline".

On page 19, line 25, the percentage of ZnO in the dust slurry is not given.

**Box No. VIII** Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

The following defects do not comply with PCT Article 6:

The term "treating" is vague and renders claim 1 unclear.

The term "processing" is vague and renders claims 10, 11, 16, and 17 unclear.

The ferrite and magnetite pigments in claims 23 and 27, respectively, should be defined by structure, properties and characteristics independently of the process for their manufacture. Defining the pigments in terms of their process of manufacture renders the claims unclear.

The expression "having a high resistance to leaching" is vague and renders claim 24 unclear. The word "high" is a relative term and thus can be interpreted as having various meanings.

## Supplemental Box

In case the space in any of the preceding boxes is not sufficient.

Continuation of: Box No. V

Claims 27, 28, and 30 do not comply with **PCT Article 33(2)**. The subject matter was disclosed before the claim date in D3 and D4. D3 discloses a magnetite pigment and its use as a pigment in building materials and toners. D4 discloses a magnetite pigment and its use as a pigment in plastics, plasters, concrete tiles and magnetic recording media. Although the magnetite pigments disclosed in D3 and D4 are not manufactured from EAF dust, no advantages have been disclosed in the present invention to show that a magnetite pigment manufactured from an EAF dust would have any advantages over a magnetite pigment manufactured in any other way. Furthermore, "wherein it comes from an EAF dust" is not a property of the magnetite pigment but rather a property of the process to produce the magnetite pigment. Magnetite pigments are known in the art and an allegedly new method of manufacture does not bestow patentability on an old product. Therefore claims 27, 28, and 30 are not novel.

**Inventive Step (IS)**

Claims 1-22 comply with **PCT Article 33(3)**. Document D1 is considered as describing the closest prior art. D1 discloses a hydrometallurgical process for the treatment of steel mill electric arc furnace (EAF) dust. EAF dust is washed in water to dissolve simple oxides, salts and unstable heavy oxides. The resultant solution is then decanted resulting in a supernatant liquid containing dissolved simple oxides, salts and unstable heavy metals and a slurry containing ferrites and magnetites. The slurry is then separated from the supernatant liquid. The slurry is treated using wet magnetic separation to disperse the ferrite particles from the magnetite particles. Optionally, a liquid dispersant is present during the wet magnetic separation step wherein methanol may be used as the liquid dispersant. The slurry containing ferrite particles dispersed from the magnetite particles can then be treated to produce ferrite and/or magnetite pigments for use in paints, ceramics, cement, concrete and powder metallurgy. Although D1 specifies that a liquid dispersant is present during the wet magnetic separation step, there is nothing to suggest that an anionic surfactant can be used as the liquid dispersant, nor would this be obvious from the prior art. Therefore claim 1 is considered inventive. Claims 2-22 are dependent on claim 1 and, as such, are also considered inventive.

Claims 23-30 do not comply with **PCT Article 33(3)**. Since the subject matter of claims 23-30 is not new, claims 23-30 cannot be considered inventive.

**Industrial Applicability (IA)**

The subject matter of claims 1-30 is considered to be industrially applicable and thus fulfills the requirements of **PCT Article 33(4)**.

**A HYDROMETALLURGICAL SEPARATION PROCESS OF STEEL MILL  
ELECTRIC ARC FURNACE (EAF) DUST AND THE PIGMENTS OBTAINED BY  
THE PROCESS**

5

**FIELD OF THE INVENTION**

The present invention relates generally to the field of steel mill dust treatment. More particularly, the invention comprises a hydrometallurgical separation process of dust produced by electric arc furnaces in steel mills. This process permits, on one hand, the decontamination of the dust and on the other hand, the  
10 production of ferrite and/or magnetite pigments useful in paints, plastics and concrete. The invention also comprises the pigments produced from this process.

**PRIOR ART**

Electric arc furnace (EAF) dust, also known under the name of (K061), is classified as a dangerous material because it contains high concentrations of  
15 soluble heavy metals such as cadmium, zinc, chromium and lead, but in particular lead. More specifically, EAF dust usually contains more than 5 ppm soluble lead and hence, does not meet the limits of lead specified by TCLP (Toxicity Characteristic Leading Procedure). This dust also contains spinel compounds, notably magnetite ( $\text{Fe}_3\text{O}_4$ ) and diverse ferrites ( $\text{MO}_2\text{Fe}_2\text{O}_3$ ). These spinel  
20 compounds as well as contaminants appear in the form of agglomerates and aggregates. To the naked eye, the dust is brown and an observer, even with the aid of a magnifying glass, will not notice the presence of black balls of magnetite, even if certain black balls can attain 150 $\mu\text{m}$  in diameter. The brown ferrite contained in the dust is ultrafine, and as a pigment, coats by adsorption the larger  
25 particles of magnetite.

Table 1 shows the typical chemical composition of EAF dust coming from two distinct steel mills. These compositions show elevated concentrations of certain heavy metals.

c) separating the slurry and the supernatant liquid;

d) adding to the slurry obtained in step c) an anionic surfactant to disperse the ferrite particles adsorbed on the magnetite particles; and

5 e) treating the slurry from step d) to produce pigments selected from the group consisting of ferrite pigments, magnetite pigments and ferrite/magnetite pigments.

Preferably, the sequence of steps a) to c) is performed more than one time before adding the anionic surfactant.

10 The use of an anionic surfactant was found to increase the efficiency and quality of further separation steps such as screening, and ferrite/magnetite separation by a magnetic separator. Steps a) to c) also enable the decontamination of the dust by leaching salts, metals and simple oxides such as lead oxide. This selective solubilization is due to the alkaline pH solution, which is preferably greater than 12, resulting from the first washing, and optional second washing, with water. This alkalinity promotes the solubilization of PbO and, with the addition of surfactant, 15 enables the product to pass the test set out by the TCLP, which regulates standards of dangerous materials.

Advantageously, the process of the invention also enables the separation of the ferrites from the magnetites without breaking the cristallographic structure of the spinels, so as to produce magnetite and/or ferrite pigments of different grades, 20 whose different compositions have commercial values.

The process also permits the decontamination of EAF dust by hydrometallurgical means while maintaining the most stable families of spinels intact.

The solution obtained is step a) described above has a positive zeta potential, and the anionic surfactant is preferably added in a concentration sufficient to reduce 25 the zeta potential to or close to the isoelectric point, and more preferably to the isoelectric point.



surface characteristics. In many cases, specific coating also gives the pigments even greater specific properties for more particular markets.

5 The novelty of the process for all grades of pigment resides in an initial treatment of the EAF dust with water with the addition of an anionic surfactant. This surfactant increases the efficiency and quality of the ferrite/magnetite separation by the magnetic separator. This initial treatment also enables the decontamination of the dust by leaching salts, metals and simple oxides such as lead oxide. This selective solubilization is due to the alkaline  $\text{pH} > 12$  solution resulting from the first washing (first mixing) and rinsing (second mixing) with water (Table 2). This  
10 alkalinity promotes the solubilization of  $\text{PbO}$  and enables for the product to pass the test set out by the TCLP, which regulates standards of dangerous materials (Table 3).

### **Ferrite pigments**

#### **First grade (F1)**

The ferrite pigment of the first grade was produced with the aid of a solution containing an optimal concentration of surfactant, the concentration being a  
5 function of the isoelectric point of the dust to be treated, and with a leaching hereafter referred as to the second treatment with water only.

The first grade ferrite pigment contained a high quantity of lead that cannot be easily leached under normal pH conditions. After ten months and many agitations in water, this pigment showed no leaching of heavy metals (Table 4) and is  
10 comparable to pigments of the second and third grade described below. Heavy metals, with the exception of 8% zinc in the resistant form of zincite, were present and stabilized in the structure of certain ferrites and spinels.

The varied acid leaching steps of the process left solid ferrites of varied compositions and, as experience has taught, the ferrites rich in Ca were less stable to leachings than zinc ferrites or other ferrites representing complex oxides of Ca, Fe, Zn, Mn, Mg, Ni, Cr, etc. The resistant ferrites left after leaching, which  
5 made up the pigment, gave the pigment a high thermal stability and resistance to leaching, which are a function of the ionic stoichiometry and of the type and quality of the composite cristalline structures.

On the other hand, the ferrite pigments of the first grade demonstrated high  
10 resistance to corrosion as demonstrated in the salt spray (mist) tests, allowing coated metallic plates to resist corrosion for more than 1500 hours in a salt mist, which is equal or superior to all other pigments, including those of commercial quality used in the tests.

The first grade ferrite pigment owes its corrosion (salt mist) resistance to CaO, which is sacrificed as  $\text{Ca(OH)}_2$  and/or to the resulting alkaline viscosity (soapy appearance) associated with  $\text{Ca(OH)}_2$  and the pigment's elevated alkalinity.  
15

#### Second grade (F2)

The ferrite pigment of the second grade was produced in the same way as the first grade, except that the second treatment was performed with sulphuric acid.

20 The preparation steps for the second grade pigments were identical to those used for the ferrite pigments of the first grade, the addition of the surfactant occurring after the first washing but before the magnetic separation. For the second grade pigments, leaching using sulphuric acid at a pH between 0,5 and 3 allowed for the preservation of a certain quantity of hydrated calcium sulphate, the solubilization  
25 of all the Zn in the form of zincite ( $\text{ZnO}$ ) and the stabilization of lead as a solid sulphate. Using this treatment, the effluents rich in zinc sulphate, are a suitable form of compound to be directly recycled back into an electrolysis process, in order to recuperate the value of the zinc. The calcium sulphates generated by the

industrial market. This grade of pigment showed enhanced resistance to corrosion depending on the coating used and also displayed a thermal stability as they preserve their colour tint at temperatures exceeding 300 to 400°C.

**TABLE 5**

**5      E VARIATION OF FERRITE HS4 PIGMENTS (THIRD GRADE) FROM MILL 1**

FM #	COLOR			Delta E
	L	a	b	
1317	27.13	2.27	7.38	0.2
1318	27.1	2.36	7.35	0.15
1319	26.81	2.34	7.15	0.21
1320	26.82	2.4	7.25	0.17

This thermal resistance is a requirement for plastics, powdered paint and ceramics.

Fourth grade (F4)

- 10      The ferrite pigment of the fourth grade was produced in the same way as the third grade, with the addition of a wet grinding step.

This pigment can be used in concrete as a cement additive that increases the fluidity and compression resistance of the concrete. This pigment had a finer granulometry than the third grade, ferrite pigment and the ferrite/magnetite pigment.

15

The ferrite pigments of the first, second, third and fourth grades have applications in anticorrosive paints. The third grade can be used in plastics and powder paints due to its thermal resistance. This pigment can also be used as a cement additive, thinning agent and additive in high performance concrete. The major difference

After the first treatment which is performed in the tank (10) of figures 1 to 6, the slurry (16) is either sent to the magnetic separation (20) to separate the magnetite particles and the ferrite particles, as in figures 1 to 5, which show the first to sixth  
5 variants; or it is sent to screening (30) and thereafter to the second treatment (40), as in figure 6 which shows the seventh variant, to ultimately produce a pigment of ferrite and magnetite suitable for use as a colorant for concrete.

The first to the sixth variants, which concern the production of ferrite pigments (figures 1 to 4) and the production of magnetite pigments (figure 5), will now be  
10 described in further detail while referring to figures 1 to 5. For each of these variants, as broadly described, the slurry (16) from the first treatment was subjected to a magnetic separation (20) to obtain a ferrite fraction (24) and a magnetite fraction (26). Both these fractions (24 and 26) were respectively subjected to a screening (30 or 300).

Referring to figures 1 to 4, the refined ferrite fraction (34) from the screener (30) was further subjected to a second treatment (40) depending on the grade of ferrite pigments produced. In the case of the third and fourth variants (figs 3 and 4), the second treatment was preceded by at least one of the following steps: decantation (60), grinding (50 or 55), and magnetic separation (200). After the second  
20 treatment (40), the slurry (46) obtained was subjected to filtration (70), and thereafter to the typical process steps used in the field of pigment production, as for example drying (90), coating (80) and micronization (100).

The filtration step (70) produces water to be recycled (72).

It is also worth mentioning that in the first and the third process variants, the  
25 second treatment was preferably followed by a second magnetic separation (200, 220) used to separate the magnetite fraction (202, 222) that remained in the slurry (46) from the ferrite fraction (206, 226). The ferrite fraction (206, 226) was sent

back to the ferrite production line for producing the ferrite pigments, whereas the magnetite fraction (202, 222) was sent to the magnetite production line.

Referring to figure 5, the magnetic fraction (26) from the magnetic separation (20) was sent, preferably with magnetic particles (202, 212, 222) from other steps of the process, to a first screening (30) at 150  $\mu\text{m}$ . The fraction (38) of less than 150  $\mu\text{m}$  was sent to a ball mill (500) and then to a second screening (300) to obtain a first finer fraction (304) with particles having a grain size of 6  $\mu\text{m}$  or less; and a coarser fraction (306) with particles having a grain size greater than 6  $\mu\text{m}$ . The coarser fraction (306) was then milled and screened at 40  $\mu\text{m}$  (these steps are not shown on figure 5) to finally obtain a coarser fraction containing particles having a grain size between 40 and 6  $\mu\text{m}$ .

The coarser fraction (306) was wet grinded by attrition (50) to attain a mean grain size of approximately 0,3  $\mu\text{m}$ . It was thereafter subjected to the typical process steps used in the field of pigment production, as for example drying (90), coating (80) and micronization (100).

The finer fractions (304) were purified by suspending (600) residual contaminants contained therein with an anionic surfactant (802), to obtain a purified magnetic fraction (602).

#### **MAGNETIC SEPARATION (20)**

The magnetic separation step (20) yields the first fraction (24) containing in a major portion ferrite particles and the second fraction (26) containing in a major portion magnetite particles.

In the raw EAF dust, the black magnetite is never apparent or visible to the naked eye, even though the magnetite is large and rough compared to the other

Another indication of the efficiency of the separation is provided by the results of the tests of recuperation of magnetite obtained from the rough fraction  $\geq 20\mu\text{m}$  after screening the non magnetic fraction. This ferrite fraction comprised rough contaminants (i.e. coal) and magnetite, with a smaller amount of fine silica and carbonates or calcium phases. The magnetite was not separated in the first magnetic separation as it was coated with silica and phases of calcium. The trapped quantity varied with the quantity and concentration of the added surfactant. For a separation without surface active, 197 g of rough magnetite was recovered. The same fraction after having added the surface active resulted in a recuperation of 221 g, or 11% more magnetite recovered. This result is explained by the fact that the surface active is more efficient in dispersing fine particles, and thus the finer contaminants from the larger spheroids of magnetite; coal does not influence the separation.

For the process according to the invention, it is preferable to use the surfactant according to a specific dosage in order to produce two fractions (24 and 26) that are adequate for realizing products suitable for commercial applications, as will be explained in more details further below.

### **SCREENING (30 or 300)**

Screening of the ferrite fraction (24) or the magnetic fraction (26) is essential to produce ferrite pigments or magnetic pigments having a commercial value, because it allows the physical separation of larger agglomerates and certain contaminants accompanying the ferrites and magnetites. All particles or agglomerated substances of more than  $20\mu\text{m}$  with or without magnetic susceptibility, can be separated. Coal and even partially fused scrap metal fragments are separated by screening.

In addition to improving the separation of the ferrites and magnetites in the first treatment and the magnetic separation, the addition of surfactant prevents the clogging of the screens and enables screening with openings of 20 to  $6\mu\text{m}$ . The clogging is caused by portlandite, a calcium hydroxide  $\text{Ca(OH)}_2$ , which is

As an example, the effect of the second treatment is illustrated in Table 10 by the variation of lead for the different third grade pigment leached at different pHs with nitric acid. The most important variations are the lead concentrations and the zeta for the different pigments. The sign of the relative charge represented by the zeta potential in aqueous medium is particularly important, the latter changing from +40mV for the first grade to -9 to 11 mV for the leached pigment at a pH of 1,5 to 0,5. This parameter is important for the behavior of the pigment and also influences the pigmentary properties and the coating mechanism, or even the type of coating it can accept, if required.

#### 10 Conditions for the second treatment (40)

A pulp of 8 to 10% solids in 55 liters of water was acidified with nitric acid 6 N to the desired pH by continuous addition of acid for a period of 30 min. The pH was maintained for 60 min. by sporadically adding the acid while agitating the pulp. Decantation was preferred and the supernatant liquid was removed.

15 In the first variant, simply water (37) is used as the leaching agent. In the second variant, sulfuric acid (42) is used, and in the third variant, nitric acid (43) is used as the leaching agent.

#### PRODUCTION OF FERRITE/MAGNETITE PIGMENTS (SEVENTH VARIANT)

Referring to figure 6, and in accordance with the seventh variant used to produce ferrite/magnetite pigment, the slurry (16) from the first treatment (10) was not subjected to magnetite separation. The slurry was rather subjected to a screening at the 60  $\mu$ m or less. The coarser fraction (31) was separated into higher-magnetic (216) and lower-magnetic (218) fractions, by magnetic separation (220), and these fractions could be used in other parts of the process. The finer fraction, hereinafter referred as to the refined slurry (33) was subjected to the second leaching treatment (40) with nitric acid (43) at a pH of about 3, to obtain a leached slurry (48) with no or a controlled amount of ZnO which retards the setting of concrete. The leached slurry (48) was separated into a solid fraction (74)



containing a mixture of ferrite and magnetite pigments and a liquid fraction (72) containing constituents soluble in nitric acid. The solid fraction (74) was then dried (90) to obtain dry pigments containing a mixture of ferrite and magnetite.

5 **SPECIFIC CHARACTERISTICS OF THE FERRITE PIGMENT OF THE THIRD GRADE**

The pigmentary properties for the ferrite pigments of the third grade are shown in Table 11 along with the commercial pigments recognized as ferrites. These commercial ferrites are obtained by mixing oxides according to a company-specific formulation and then calcining at high temperature. The table shows  
10 different important quantitative pigmentary properties such as:

- pH;
- humidity;
- "long oil" absorption ;
- 15 • dry colour of pigment;
- paint colour;
- gloss;
- dispersion on the Hegman gage;
- resin incorporation time

**CLAIMS**

1. A hydrometallurgical process for the treatment of steel mill electric arc furnace (EAF) dust containing agglomerates of small ferrite particles and larger magnetite particles, the ferrite particles coating by adsorption the larger magnetite particles,  
5 the dust further containing calcium oxide, zinc oxide and a toxic amount of leachable lead together with minor elements selected from the group consisting of Mg, Cr, Cu, Cd, V, and chlorides, the process comprising the steps of:
- a) washing the EAF dust in water to dissolve soluble salts, metals and simple oxides contained in the dust, said washing step being performed under  
10 agitation and with an alkaline pH;
  - b) decanting the solution of step a) to obtain a supernatant liquid containing the dissolved salts, metals and simple oxides, and a slurry containing ferrites and magnetites, a non toxic amount of leachable lead and a reduced amount of calcium;
  - 15 c) separating the slurry and the supernatant liquid;
  - d) adding to the slurry obtained in step c) an anionic surfactant to disperse the ferrite particles adsorbed on the magnetite particles; and
  - e) treating the slurry from step d) to produce pigments selected from the group consisting of ferrite pigments, magnetite pigments and ferrite/magnetite  
20 pigments.
2. The process according to claim 1, wherein the sequence of steps a) to c) is performed more than one time before adding the anionic surfactant.
- 25 3. The process according to claim 1 or 2, wherein the solution obtained in step a) has a positive zeta potential, and the anionic surfactant is added in a concentration sufficient to reduce said zeta potential to or close to the isoelectric point.
- 30 4. The process according to claim 3, wherein said zeta potential is reduced to the isoelectric point.

5. The process according to any one of claims 1 to 4, wherein the anionic surfactant is a phosphate or an equivalent thereof.

5 6. The process according to any one of claims 1 to 5, wherein the anionic surfactant preferred is sodium metaphosphate.

7. The process according to any one of claims 1 to 6, wherein step e) of treating the slurry comprises the step of:

10 - magnetically separating the slurry into a first fraction composed essentially of brownish ferrites and a second fraction composed essentially of black magnetite, the first fraction being less magnetic than the second fraction.

8. The process according to claim 7, wherein the step of magnetic separation is  
15 performed with a magnetic field in the range of 400 to 700 gauss.

9. The process according to claim 8, wherein the magnetic field is around 550 gauss.

20 10. The process according to any one of claims 7 to 9, further comprising the step of:

-processing the first fraction to produce ferrite pigments.

11. The process according to claim 10, wherein the step of processing the first  
25 fraction comprises:

-removing from the first fraction, particles having a grain size of 20  $\mu\text{m}$  or more, to obtain a refined first fraction

-leaching said refined first fraction with a solvent, to obtain a leached slurry;

-separating said leached slurry into a solid fraction containing ferrite  
30 pigments and a liquid fraction containing constituents of the first fraction soluble in said solvent; and

- drying said solid fraction to obtain dry pigments of ferrites.

12. The process according to claim 11, wherein the solvent is water and the ferrite pigments are ferrite pigments of a first grade.

5

13. The process according to claim 11, wherein the solvent is sulphuric acid, the leaching is performed at a pH of 0,5 to 3 and the ferrite pigments are ferrite pigments of a second grade.

10 14. The process according to claim 11, wherein the solvent is nitric acid, the leaching is performed at a pH of up to 3, and the ferrite pigments are ferrite pigments of a third grade.

15 15. The process according to claim 14, comprising the step of wet grinding the solid fraction to obtain a forth grade of pigments having a finer mean grain size and a lower concentration of lead as compared to the ferrite pigments of the third grade.

20 16. The process according to any one of claims 7 to 15, comprising the step of:  
-processing the second fraction to produce magnetite pigments.

17. The process according to claim 16, wherein the step of processing the second fraction comprises the step of:

25 -screening at 6  $\mu\text{m}$  to obtain a first finer fraction with particles having a grain size of 6  $\mu\text{m}$  or less; and a coarser fraction with particles having a grain size greater than 6  $\mu\text{m}$ .

18. The process according to claim 17, comprising the steps of

30 -milling said coarser fraction, and  
-removing from the milled coarser fraction the particles having a grain size greater than 40  $\mu\text{m}$  and returning said particles for further milling, and a second

finer fraction having particles with a grain size of less than 6  $\mu\text{m}$ , resulting in said coarser fraction containing particles having a grain size between 40 and 6  $\mu\text{m}$ .

19. The process according to claim 17 or 18, wherein it comprises the steps of:

- 5           - wet grinding by attrition the coarser fraction to attain a mean grain size of approximately 0,3  $\mu\text{m}$ ; and  
          -filtering and drying the grinded coarser fraction, to obtain a magnetite pigment of a first grade.

10   20. The process according to any claim 17 or 18, wherein it comprises the step of:

- purifying the first and second finer fractions by suspending residual contaminants contained therein with an anionic surfactant, to obtain a purified magnetic fraction;  
          -decanting the purified fraction;  
15       - wet grinding by attrition the purified fraction; and  
          - filtering and drying the ground purified fraction, to obtain a magnetite pigment of a second grade.

21. The process according to claim 1 or 2, comprising the steps of:

- 20       -removing from the slurry obtained in step d), particles having a grain size of 60  $\mu\text{m}$  or less, to obtain a refined slurry;  
          -leaching the refined slurry with nitric acid at a pH of about 3, to obtain a leached slurry with no or a controlled amount of ZnO which retard the setting of concrete;  
25       -separating said leached slurry into a solid fraction containing a mixture of ferrite and magnetite pigments and a liquid fraction containing constituents soluble in nitric acid; and  
          - drying said solid fraction to obtain dry pigments containing a mixture of ferrite and magnetite.

30

22. A process according to any one of claims 10 to 21, comprising the steps of:  
-coating said pigments with an inorganic and/or organic coating; and  
-micronizing the coated pigments.

5 23. A ferrite pigment obtained by a process according to any one of claims 10 to 15.

24. A ferrite pigment coming from an EAF dust and having a high resistance to leaching.

10

25. A ferrite pigment according to claim 24, wherein it shows a color thermal stability at temperatures of 300°C and higher.

15 26. A ferrite pigment according to claims 24 or 25, wherein it provides anticorrosion properties to metallic paint formulation.

27. A magnetite pigment obtained by a process according to any one of claims 16 to 20.

20 28. A magnetite pigment, wherein it comes from an EAF dust.

29. Use of a ferrite pigment according to any one of claims 23 to 26 for incorporation in an anticorrosive paint formulation, plastic formulation or concrete formulation.

25

30. Use of a magnetite pigment as defined in claim 27 or 28, for incorporation in a paint formulation, plastic formulation or toner formulation to provide magnetic properties.

**Figure 1**

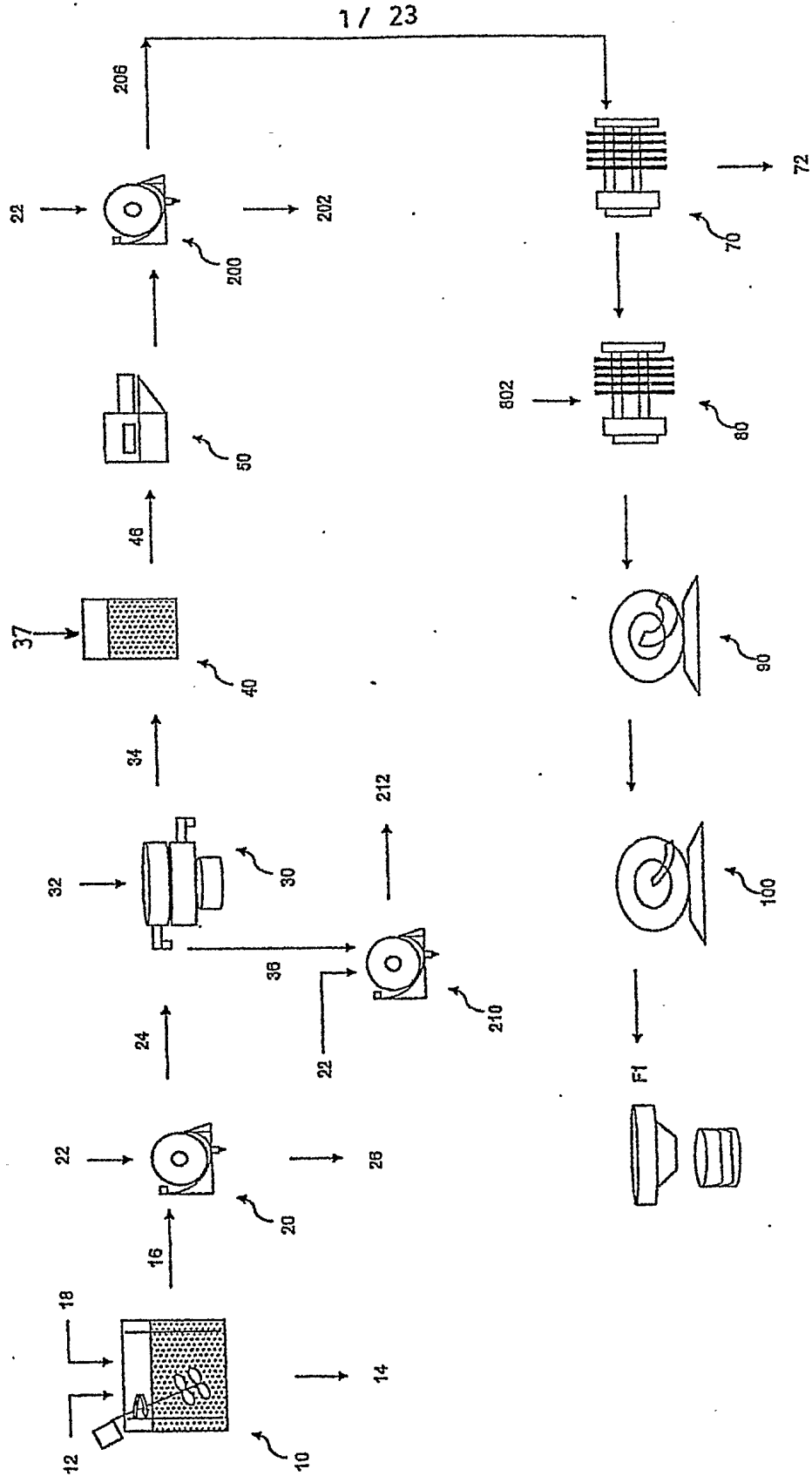


Figure 2

